

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Christoph Briehn et al.

Group Art Unit: 4171

Examiner: Hannah J. Pak

Serial No.: 10/599,285

Filed: September 25, 2006

For: CURABLE COMPOSITION CONTAINING
SURFACE-MODIFIED PARTICLES

Attorney Docket No.: WAS 0807 PUSA

**DECLARATION OF DR. CHRISTOPH BRIEHN
UNDER RULE 37 C.F.R. § 1.132**

Commissioner for Patents
U.S. Patent & Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Christoph Briehn, do hereby declare and state as follows:

1. I am a coinventor of the subject matter of U.S. Application Serial No. 10/599,285, and am familiar with the contents of the application, the claimed subject matter, the recent Office Action dated December 3, 2009, and the cited prior art, Fukushima et al. US. 6,306,502.

2. I studied chemistry at the Technischen Hochschule, Darmstadt from 1993 to 1995, and upon graduation, pursued further studies in chemistry at the Universität Würzburg, from which I obtained my Diploma in Chemistry in 1998. I then pursued my Ph.D. in organic chemistry at the Universität Ulm, where my thesis was entitled "Towards Combinatorial Synthesis and Screening of Organic Conjugated Materials: Quater (3-

arylthiophene)s." I graduated *summa cum laude* in October of 2001. I pursued post-doctoral studies at the California Institute of Technology from December of 2001 to January of 2003.

In 2003, I accepted employment at the Consortium for Electrochemical Industry, Munich, a research cell of Wacker Chemie AG, and have been a work group leader from 2003 to the present.

I am very familiar with organosilicon chemistry, including the use of silanes and siloxanes, the preparation and use of modified silicas, and with polymer-based coating systems, and in particular, abrasion resistant coatings. I am an inventor or coinventor of patents and patent publications in at least 15 different patent families, filed in numerous countries, a copy of which is appended hereto.

3. Based upon my experience in the field of abrasion resistant coatings, I am aware that those skilled in the art have long sought coatings which are increasingly abrasion resistant. Abrasion resistant coatings which are also transparent rather than cloudy or opaque have also been desired. Abrasion resistant inorganic coatings of silica, silicon carbide, or diamond have also been proposed. For example, diamond coating of optical glass used in eyeglasses is known. However, it should be obvious that these coatings are not suitable for many applications, for example due to their method of production, or due to their physical characteristics, including freedom from brittleness and differences in the coefficient of thermal expansion between the coating and the substrate. Thus, curable coatings based on polymers have been widely used. For example, curable polyacrylate coatings based on addition-polymerizable or photocurable (meth)acrylate-functional monomers such as hexanedioldiacrylate, glycerol triacrylate, and the like have long been used. Increasing the crosslink density by use of higher functionality acrylates is known to increase the hardness of these coatings.

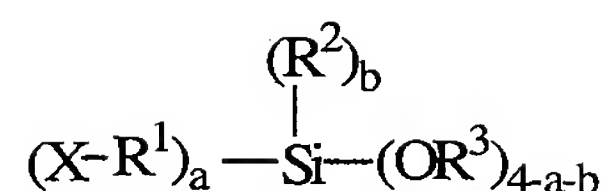
However, the hardness acquired, even using highly functional monomers, is still insufficient for many applications, such as automotive clear coats and abrasion resistant coatings on headlight and taillight assemblies, to name but a few. To increase hardness and scratch resistance, it has been long proposed to add finely divided hard fillers such as silica to

the compositions. However, this approach turned out to be problematic for numerous reasons, and also failed to offer satisfactory increases in abrasion resistance. This is illustrated in the present application by Comparative Example 1, which employed a silica organosol and hexanediol diacrylate. The loss of gloss was *circa* 78% in the Peter-Dahn scratch test.

As long ago as at least 1977, as disclosed in French et al. U.S. Patent 4,006,271 (cited by *Fukushima*), a silica organosol was prepared by acid hydrolysis of methyltrimethoxysilane and then modified by addition of an aminoalkylalkoxysilane. However, as indicated by *Fukushima* (column 1, lines 40 - 54), such coatings are not satisfactory. *Fukushima* also discusses numerous other prior art methods of producing hard, abrasion resistant coatings in columns 1 and 2, and discusses their deficiencies.

Fukushima and the patents cited therein as well as those cited by the Patent Examiner during prosecution of the *Fukushima* patent testify to the long felt need in the industry for abrasion resistant coatings. A search of the patent and non-patent literature would provide conclusive evidence that the search for improved abrasion resistant coatings continues to this day. See, *e.g.* U.S. Patents 7,524,562 and 7,476,415 and U.S. published application 2009/0297839, all of which are directed to providing abrasion resistant coatings. One skilled in the art is very much aware of the long felt and continuing need for abrasion resistant coatings. Those skilled in the art, including the coinventors of the present application, were aware of the *Fukushima* reference. This reference was initially published in 1997 in Japan. Others skilled in the art were no doubt aware of this reference as well. Yet despite the some seven years between the publication of *Fukushima* and our invention, no one proposed the scratch resistant coatings we invented. *Fukushima* does not direct the skilled artisan to the claimed invention.

4. *Fukushima* discloses unique coatings based on (meth)acrylate-functional isocyanurates and alicyclic urethane poly(meth)acrylates. Into this radical-polymerizable base composition is added particulate silica conventionally modified by reaction with a compound (I) of the formula



or a hydrolysis product thereof. In this formula, in the relevant portions thereof, R^1 is an "alkylene" group with 0 - 8 carbons, *i.e.* a covalent bond or a C_{1-8} alkylene group, and X is an acrylo, methacrylo, or vinyl radical.

In the claimed invention, the silane which modifies the silica has the formula



where A is an electronegative O, S, $=NR^4$ or $=N-(D-C)$ group, while the combination of "D-C" contains an ethylenically unsaturated group, and D may be, *inter alia*, a carbonyl group. Thus, included within the grouping "-A-D-C" are (meth)acrylate groups, vinyl ether groups, and the like. However, the grouping "-A-D-C" does not, for example, include vinyl groups.

In the claimed invention, it is necessary that the unsaturated "-D-C" group be isolated from the silicon atom by a $-CR^3_2-A-$ group. These alkoxysilanes are termed " α -silanes", and behave significantly differently from other silanes which do not have a $-CR^3_2-$ methylene or substituted methylene group (hereinafter, just "methylene" for simplicity) as a "spacer" between the electronegative A group and silicon.

Fukushima does not direct the skilled artisan to the claimed invention, for numerous reasons. First, *Fukushima* does not even require a methylene group. A methylene group is but one of numerous possibilities, including being merely a covalent bond. *Fukushima* allows his (meth)acrylate and vinyl groups to be bonded directly to silicon. He also allows C_{2-8} alkylene "spacers" to be employed. Second, *Fukushima* does not even require an "A" group. His vinyl group, again, for example, may be bonded directly to the silicon. Vinyltrimethoxysilane and vinyl triethoxysilane are among his preferred silanes. See column 5, lines 21 - 28.

It is clear that while α -silanes are within the broad range of silanes disclosed by *Fukushima*, he never contemplated their use, nor had any idea of the surprising and unexpected results which occur through their use. For instance, *Fukushima* discloses 12 specific alkoxysilanes at column 5, lines 7 - 20. It is noteworthy that none of these is an α -silane. In his examples, the sole silane used is 3-methacryloxypropyltrimethoxysilane, which is not an α -silane.

Applicants surprisingly and unexpectedly discovered that when α -silanes such as 3-methacryloxymethyltrimethoxy silane are used instead of *Fukushima's* disclosed silanes, scratch resistance is markedly increased.

A direct comparison is made possible between Applicants' Example 3 on page 14 of the specification and Comparative Example B submitted in my prior Declaration under Rule 132. In these examples, the sole difference is the substitution of 3-methacryloxypropyltrimethoxysilane in the Comparative Example, as taught by *Fukushima*, with Applicants' claimed 3-methacryloxymethyltrimethoxy silane. The scratch resistance of the inventive example is 24% higher than the non-inventive comparative example. This is very surprising and unexpected. This 24% increase is truly significant, especially in view of the maturity of the art.

In Applicants other examples, it is shown that other α -silane-functionalized silicas, whether initially supplied as an aqueous dispersion or an organosol, are surprising effective in increasing scratch resistance. This is particularly striking, as even mono-alkoxy-functional α -silanes showed this improvement, as indicated by Examples 1, 2, 4, and 5.

5. The Examples and Comparative Examples provide evidence of surprising and unexpected results which on a scientific basis is commensurate with the scope of the claims.

For example, it is known that all the A groups of the claims create α -silanes of high reactivity. Thus the Examples where A is oxygen are directly supportive of other silanes where A is, for example, -S- or =NR⁴. For R¹, it is known that all -OR¹ groups are activated in α -silanes. Thus, the experimental results support a wide variety of OR¹ groups, *e.g.* methyl, ethyl, propyl, phenyl, etc. The examples include α -silanes with one OR¹ group and with 3 OR¹ groups. Both worked very well. There is no scientific reason to suspect why two OR¹ groups, halfway between these examples, would not work just as well.

On page 4 of the recent Office Action, the Examiner criticized Applicants' prior showing because the direct comparative example presented in the prior Declaration utilized a single α -silane, methacrylomethyltrimethoxysilane, and compared the results obtained when using this α -silane with methacrylopropyltrimethoxysilane, as used by *Fukushima*. As indicated above, there is no scientific reason to believe that other α -silanes would not be similarly more effective than the propyl-spaced (or ethyl-,butyl-,hexyl-spaced) alkoxysilanes disclosed by *Fukushima*. For example, methacrylomethyl-dimethylmethoxysilane, a silane with but a single methoxy group, was highly effective. In fact, Example 5 in the specification used this silane and provides the highest scratch resistance of all formulations tested.

It is well known that the activity of alkoxy silanes and their ability to crosslink increases with increasing alkoxy functionality. It is also known that conventional, non- α -silanes bearing but a single methoxy group or even two methoxy groups are very slow in reacting. Based upon my experience with alkoxysilanes, it is clear that methacrylopropyldimethylmethoxysilane would not react sufficiently to provide the necessary scratch resistance. The scratch resistance would be much less than when using methacrylomethyldimethylmethoxysilane. Nor would the nature of the methacrylo moiety make a difference. α -silanes bearing acrylo or vinyl ether groups would also provide greater scratch resistance than their non- α -silane analogues. The reaction with the silica is not through the unsaturated group, but with the alkoxy groups. The ethylenically unsaturated group only "goes along for the ride," and ultimately will addition bond to the unsaturated

groups of the polymer matrix. In this sense, even a simple vinyl group, such as a vinyl group directly connected to silicon of the alkoxysilane will work well in binding to the matrix, as evidenced by *Fukushima's* choice of vinyltrimethoxysilane and vinyltriethoxysilane as preferred unsaturated alkoxysilanes. However, such a silane with a vinyl group attached directly to silicon is not an α -silane, and thus while efficient bonding to the polymer matrix would be expected, the scratch resistance would be clearly less than the scratch resistance obtained from an α -silane.

Thus, I believe that the showings made thus far are fully commensurate with the scope of the claims, and are cogent evidence of the surprisingly and unexpectedly higher scratch resistance obtained by the use of the claimed alkoxy-functional α -silanes.

I hereby declare that all statements made herein of my knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of the application or any patent issuing thereon.

Date: _____

03/01/10



Dr. Christoph Bruehn

RESULT LIST

Approximately 51 results found in the Worldwide database for:

Wacker as the applicant AND Briehn as the inventor

Sorting criteria: **Upload Date** Priority Date Inventor Applicant Ecla

- 1 **DISPERSIBLE NANOPARTICLES**
Inventor: BRIEHN CHRISTOPH [DE] ;
BAUMANN MARTINA [DE] (+1)
EC: C09C1/30D12; C09C3/12; (+2)
Publication EP2144968 (A1) - 2010-01-20
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C09C1/30; C09C3/12; C09C1/28; (+1)
Priority Date: 2007-05-04
- 2 **ALKOXYSYLYL FUNCTIONAL OLIGOMERS AND PARTICLES
SURFACE-MODIFIED THEREWITH**
Inventor: BRIEHN CHRISTOPH [DE] ; DELICA
SABINE [DE] (+1)
EC: C08F292/00
Publication US2010004354 (A1) - 2010-01-07
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C08K9/06; C08L83/06; C08K9/00; (+1)
Priority Date: 2006-06-27
- 3 **COMPOSITIONS CONTAINING PHOSPHONATE-FUNCTIONAL
PARTICLES**
Inventor: BRIEHN CHRISTOPH [DE] ; STANJEK
VOLKER [DE] (+2)
EC: C09D5/34; C09D7/12D2B
Publication KR20090073155 (A) - 2009-07-02
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C08K9/06; C08K5/5419; C08K7/16; (+5)
Priority Date: 2006-11-10
- 4 **USE OF ORGANOSILICON COPOLYMERS AS IMPACT-
RESISTANCE MODIFIERS**
Inventor: MINGE OLIVER [DE] ; BALL PETER
[DE] (+1)
EC: C08L51/08; C08F283/12; (+1)
Publication WO2009138388 (A1) - 2009-11-19
info: Applicant: WACKER CHEMIE AG [DE] ; MINGE
OLIVER [DE] (+2)
IPC: C08F283/12; C08F290/06; C08F290/14;
(+23)
Priority Date: 2008-05-16
- 5 **CURABLE POLYMER MIXTURES**
Inventor: BRIEHN CHRISTOPH [DE] ;
BORTENSCHLAGER MARTIN [DE]
EC: Applicant: WACKER CHEMIE AG [DE] ; BRIEHN
CHRISTOPH [DE] (+1)
IPC: C07F7/00; C07F7/00
Publication WO2009103604 (A1) - 2009-08-27
info: Priority Date: 2008-02-20
- 6 **PARTICLES COMPRISING ZWITTERIONIC STRUCTURAL
ELEMENTS**
Inventor: BRIEHN CHRISTOPH [DE] ;
BAUMANN MARTINA [DE] (+3)
EC: C08K9/06
Publication KR20080068883 (A) - 2008-07-24
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C08K9/06; C08J3/12; C08K5/16; (+3)
Priority Date: 2005-10-27
- 7 **LAYERS MADE OF HETEROSUBSTITUTED SILSESQUIOXANES**
Inventor: MAURER ROBERT [DE] ; BRIEHN
CHRISTOPH [DE] (+3)
EC: C09D183/04; C08G77/02; (+1)
Publication WO2008107331 (A1) - 2008-09-12
info: Applicant: WACKER CHEMIE AG [DE] ;
MAURER ROBERT [DE] (+4)
IPC: C09D183/04; C07F7/21; C08G77/02; (+4)
Priority Date: 2007-03-05
- 8 **PAINTS CONTAINING PARTICLES**
Inventor: STANJEK VOLKER [DE] ; SCHAUER
FELICITAS [DE] (+2)
EC: C09D7/12D2B
Publication KR20080029004 (A) - 2008-04-02
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C09D7/12; C08K9/06; C09D7/12; (+1)
Priority Date: 2005-07-22
- 9 **PAINTS COMPRISING PARTICLES**
Inventor: BRIEHN CHRISTOPH [DE] ; STANJEK
VOLKER [DE] (+2)
EC: C09D7/12D2B
Publication KR20080027953 (A) - 2008-03-28
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C09D133/04; C09D133/04
Priority Date: 2005-07-22
- 10 **PARTICLE-CONTAINING COATS**
Inventor: BRIEHN CHRISTOPH [DE] ; STANJEK
VOLKER [DE] (+3)
EC: C09D7/12D2B; C08G18/38N; (+3)
Publication KR20080031433 (A) - 2008-04-08
info: Applicant: WACKER CHEMIE AG [DE]
IPC: C09D7/12; C08K9/06; C09D7/12; (+1)
Priority Date: 2005-07-22

11 DISPERSIBLE NANOPARTICLES

Inventor: BRIEHN CHRISTOPH [DE] ;
 BAUMANN MARTINA [DE] (+1)
EC: C09C1/30D12; C08G18/28D5F; (+9)
Publication WO2008055817 (A2) - 2008-05-15
info: WO2008055817 (A3) - 2008-07-24
Applicant: WACKER CHEMIE AG [DE] ; BRIEHN
 CHRISTOPH [DE] (+2)
IPC: C09C1/30; C09C1/28
Priority Date: 2006-11-10

12 HYDROXYALKYL-FUNCTIONALIZED FILLERS

Inventor: SCHAEFER OLIVER [DE] ; BRIEHN
 CHRISTOPH [DE] (+1)
EC: C09C1/30D12; C08K9/04; (+2)
Publication KR20070100418 (A) - 2007-10-10
info:
Applicant: WACKER CHEMIE AG [DE]
IPC: C08K5/5415; C09C1/00; C09C1/36; (+5)
Priority Date: 2005-02-03

**13 PREPARATION OF ACID DERIVATIVE-FUNCTIONAL
 ORGANOSILICON COMPOUNDS**

Inventor: BRIEHN CHRISTOPH [DE] ; STANJEK
 VOLKER [DE] (+2)
EC: C07F7/18C9B; C08G77/388
Publication WO2008015123 (A1) - 2008-02-07
info:
Applicant: WACKER CHEMIE AG [DE] ; BRIEHN
 CHRISTOPH [DE] (+3)
IPC: C07F7/18; C08G77/388; C07F7/00; (+1)
Priority Date: 2006-08-03

14 ?5-Si - SILICATE-FUNCTIONAL PREPOLYMERS

Inventor: BRIEHN CHRISTOPH [DE] ; STANJEK
 VOLKER [DE] (+2)
EC:
Publication WO2008015120 (A1) - 2008-02-07
info:
Applicant: WACKER CHEMIE AG [DE] ; BRIEHN
 CHRISTOPH [DE] (+3)
IPC: C08G77/50; C08G77/00
Priority Date: 2006-08-01

**15 METAL OXIDES COMPRISING A PERMANENT POSITIVE
 SURFACE CHARGE OVER A WIDE PH RANGE**

Inventor: GOTTSCHALK GAUDIG TORSTEN
 [DE] ; BRIEHN CHRISTOPH [DE]
EC: C09C1/30D12; C01B13/14B; (+1)
Publication KR20070092251 (A) - 2007-09-12
info:
Applicant: WACKER CHEMIE AG [DE]
IPC: G03G9/097; G03G9/08; G03G9/097; (+1)
Priority Date: 2004-12-01

Data supplied from the espacenet database — Worldwide